

# An Edge-Enhancing Crystal Growth Instability Caused by Structure-Dependent Attachment Kinetics

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**Abstract.** We describe a novel crystal growth instability that enhances the development of thin edges, promoting the formation of plate-like or hollow columnar morphologies. This instability arises when diffusion-limited growth is coupled with structure-dependent attachment kinetics, specifically when the nucleation barrier on a facet surface decreases substantially as the facet width approaches atomic dimensions. Experimental data are presented confirming the presence of this instability in the growth of ice from water vapor at -15 C. We believe this edge-enhancing effect plays an important role in determining the growth morphologies of atmospheric ice crystals as a function of temperature, a phenomenon that has been essentially unexplained for over 75 years. Our model of structure-dependent attachment kinetics appears to be related to surface melting, and thus may be present in other material systems, whenever crystal growth from the vapor phase occurs near the material melting point.

## 1 Introduction

The formation of crystalline structures during solidification yields a fascinating variety of morphological behaviors, resulting from the sometimes subtle interplay of non-equilibrium surface processes at the molecular scale. In many cases, seemingly small changes in molecular dynamics at the nanoscale can produce large morphological changes at all scales. Some examples include free dendritic growth from the solidification of simple liquids, where slight anisotropies in the interfacial surface energy determine the overall characteristics of the growth morphologies [1, 2], whisker growth from the vapor phase initiated by single screw dislocations and other effects [3], the formation of porous aligned structures from directional freezing of composite materials [4], and a range of other pattern formation processes [5, 6]. Since controlling structure formation during solidification has application in many areas of materials science, much effort has been directed toward better understanding the underlying physical effects and their interactions.

One oft-studied example is the formation of ice crystals from water vapor in an inert background gas. Although this is a relatively simple physical system, ice crystals exhibit a remarkable variety of columnar and plate-like forms, and much of the phenomenology of their growth remains poorly understood [7]. Because ice plays important roles in many environmental and biological processes, understanding the detailed molecular structure and dynamics of the ice surface has received significant attention [8, 9, 10]. The present study was undertaken to use ice crystal growth from water vapor as essentially an experimental probe of the ice surface dynamics under changing conditions. In this regard we are using ice as a convenient test crystal, with our overarching goal being to better understand the molecular dynamics that govern crystal growth behaviors more generally.

Observations of ice crystal growth from water vapor dating back to the 1930s [7, 11] have revealed a complex and puzzling morphological dependence on temperature. Under common atmospheric con-

ditions, for example, ice crystals typically grow into thin plate-like forms near -2 C, slender columns and needles near -5 C, thin-walled hollow columns near -7 C, very thin plates again near -15 C, and columns again below -30 C. These observations are often summarized in the well-known Nakaya morphology diagram [7], and for over 75 years this remarkable behavior as a function of temperature has remained essentially unexplained. After considerable research effort, the underlying physical mechanisms that govern the morphologies of growing ice crystals remain quite poorly understood. [7, 12, 13].

The temperature dependence seen in ice growth is likely related to temperature-dependent surface melting, but even this is not known with certainty. Surface melting describes an equilibrium structural organization of the crystal surface, and its temperature dependence is itself only poorly understood [10]. How surface melting in turn affects a highly dynamical process like crystal growth is clearly a very difficult problem.

While investigating this phenomenon, we have come to realize that diffusion-limited growth coupled with the usual assumptions regarding the water vapor surface attachment kinetics cannot explain the growth of thin plate-like ice crystals. To solve this dilemma and explain the disparate growth measurements, we recently proposed that the attachment kinetics does not depend solely on temperature and supersaturation, as is typically assumed, but depends also on the morphological structure of the crystal. We refer to this phenomenon as *structure-dependent attachment kinetics* (SDAK) [14].

In this paper we better define the SDAK model, show that it leads to an edge-enhancing growth instability, and we describe experimental data and crystal growth modeling that strongly support this hypothesis. For the ice case, the evidence suggests that SDAK effects play a substantial role in determining growth morphologies, especially the formation of thin plate-like and hollow columnar crystals. For this reason, we believe the SDAK model represents a significant step toward understanding the physical basis of the Nakaya morphology diagram. Moreover, we suggest that the SDAK effect and its resulting growth instability may have more general application in crystal growth dynamics, especially when crystal growth occurs in the presence of significant surface melting.

## 2 The SDAK Model

### 2.1 Intrinsic Growth of the Principal Facets

A first step toward understanding ice crystal growth dynamics from water vapor is to quantify the growth rates of the principal facet surfaces. Following the notation in [7], we parameterize the surface growth velocities using  $v = \alpha v_{kin} \sigma_{surf}$ , where  $v$  is the perpendicular growth velocity,  $v_{kin}(T)$  is a temperature-dependent “kinetic” velocity derived from statistical mechanics, and  $\sigma_{surf}$  is the water vapor supersaturation relative to ice at the growing surface. The attachment coefficient  $\alpha$ , which depends on  $T$ ,  $\sigma_{surf}$ , and other factors, encapsulates the molecular dynamics governing crystal growth at the crystal/vapor interface. From the definition of  $v_{kin}$  we must have  $\alpha \leq 1$ .

For the simplest case – the growth of an infinite, clean, dislocation-free faceted ice surface in near equilibrium with pure water vapor at a fixed temperature – the attachment coefficient is well defined and we must have a unique  $\alpha(\sigma_{surf}, T)$  for each facet surface. We refer to the  $\alpha(\sigma_{surf}, T)$  in this ideal case as the “intrinsic” attachment coefficients for a given surface.

We determined  $\alpha(\sigma_{surf}, T)$  for the prism and basal facets through a lengthy series of measurements of crystals growing on a substrate at low background pressure. Experimental details, the

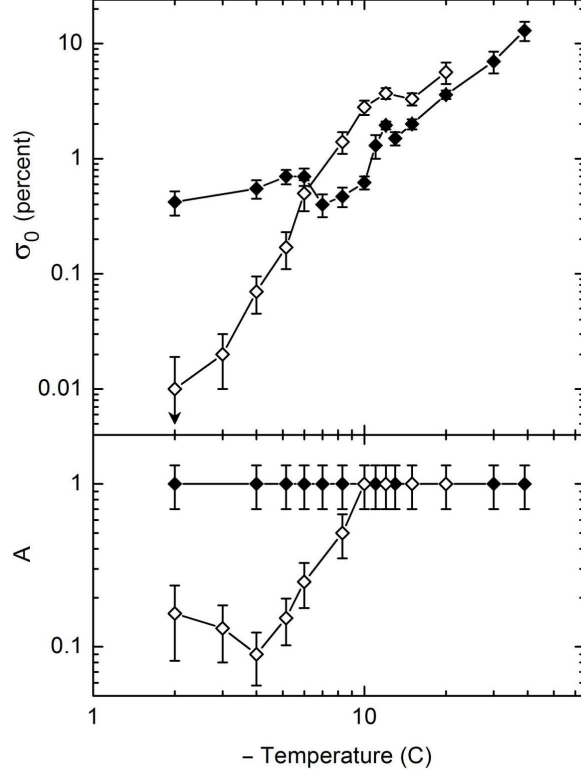


Figure 1: Measurements of the intrinsic growth rates of the principal ice crystal facets. The growth velocity normal to the surface is described by  $v = \alpha v_{kin} \sigma_{surf}$ , where  $\sigma_{surf}$  is the supersaturation at the surface and the attachment coefficient is parameterized with  $\alpha(T, \sigma_{surf}) = A \exp(-\sigma_0/\sigma_{surf})$ . The solid points show the measured  $A(T)$  and  $\sigma_0(T)$  for the basal facets, while the open points show measurements of the prism facets, from [15].

resulting data and analysis, and references to prior work measuring  $\alpha(\sigma_{surf}, T)$ , can be found in [15]. Over the temperature range  $-2 \text{ C} > T > -40 \text{ C}$ , and for both facets, our growth data are well described by a dislocation-free layer-nucleation crystal growth model, which we parameterize as  $\alpha(\sigma_{surf}) = A \exp(-\sigma_0/\sigma_{surf})$ . The measured parameters  $A(T)$  and  $\sigma_0(T)$  for the basal and prism facets are shown in Figure 1.

Note that our understanding of the detailed molecular structure and dynamics of the ice surface is not sufficient to provide an explanation for these data. The functional form for  $\alpha(\sigma_{surf})$  comes from classical nucleation theory, and this theory dictates that the parameter  $\sigma_0$  is related to the step energy  $\beta$  associated with the edge of a molecular terrace on the facet surface [15]. But the temperature dependence of  $\alpha(\sigma_{surf})$  is likely related to the details of surface melting on the two facets, for which there is only the most rudimentary theoretical description [10]. Thus for the present discussion we simply accept the measured  $A(T)$  and  $\sigma_0(T)$  in Figure 1 as empirical fact.

## 2.2 Structure Dependent Attachment Kinetics

The measured intrinsic growth rates, as parameterized above, immediately appears to contradict many details in the Nakaya morphology diagram. For example, from Figure 1 we see that  $\sigma_{0,basal} < \sigma_{0,prism}$  at -15 C, implying that  $\alpha_{prism} < \alpha_{basal}$  for all supersaturations at this temperature. This inequality suggests that columnar prisms would be the preferred growth morphology, while it is well established that thin plates form at this temperature.

The SDAK model was created to explain this discrepancy, suggesting that the attachment coefficient  $\alpha(\sigma_{surf})$  can depend on the mesoscale morphological structure of the ice surface itself. In particular, our SDAK model at -15 C assumes that  $\alpha_{prism}$  on a thin plate edge is higher than the corresponding “intrinsic”  $\alpha_{prism}$  for a large faceted surface. The increased  $\alpha_{prism}$  then reverses the above inequality, yielding  $\alpha_{prism} > \alpha_{basal}$  and resulting in the growth of thin plates.

We now carry this model one step further and propose that the increase in  $\alpha_{prism}$  on the edge of a thin plate is caused by a reduction of the nucleation barrier on that surface, specifically a reduction of  $\sigma_{0,prism}$ . More generally, we put forth the hypothesis that  $\sigma_{0,prism}$  decreases as the width of the final molecular terrace on the prism surface decreases. The same SDAK effect may be present on the basal facet as well, and its relative importance on both facets will be determined by detailed surface dynamics. After examining the physical motivation for the SDAK model in more detail, along with its subsequent ramifications, we then treat it as a testable hypothesis for comparison with experimental data.

## 2.3 SDAK Microscopic Model

As a qualitative justification for the SDAK hypothesis, consider the molecular structure and dynamics on the edge of a thin plate crystal. The radius of curvature of the edge is perhaps  $R \approx 0.5 \mu\text{m}$  for ice plates at -15 C, so the width of the last molecular terrace is roughly  $w \approx (aR)^{1/2} \approx 40a$ , where  $a \approx 0.3 \text{ nm}$  is the size of a water molecule. We might expect surface melting to be enhanced on such a narrow terrace, owing to somewhat decreased molecular binding. Since surface melting likely affects the step energy and thus  $\sigma_0(T)$ , it follows that  $\sigma_0$  may be lower on the thin crystal edge.

Looking at this from a different perspective, our measurements in Figure 1 indicate that  $\sigma_0$  generally decreases with increasing temperature on both facets. This overall trend may result from a “softening” of the step edge at higher temperatures, resulting from surface reconstruction relative to the simplest one-molecule-wide step. The fact that  $\beta \ll a\gamma$ , where  $\gamma$  is the surface energy, qualitatively supports this view [15]. If the step edge is further blurred on a thin terrace, then this would result in the proposed SDAK effect.

The SDAK hypothesis is clearly quite speculative, without a firm theoretical basis in molecular dynamics. This is necessarily the case, however, as there is no real molecular theory of surface melting and ice surface dynamics, so we cannot at present make quantitative statements about how  $\sigma_0$  should depend on surface structure. The above basic physical considerations suggest that the SDAK hypothesis is not unreasonable, and it is certainly not disallowed by molecular dynamics considerations. Note also that the growth rate of a thin crystal edge is largely determined by the attachment kinetics on the final molecular terrace. The SDAK hypothesis requires only that the molecular dynamics atop that last thin terrace be altered.

We also note that the SDAK hypothesis presents no conflict with the Gibbs-Thomson phenomenon. The latter is a well-known effect by which the equilibrium vapor pressure increases with

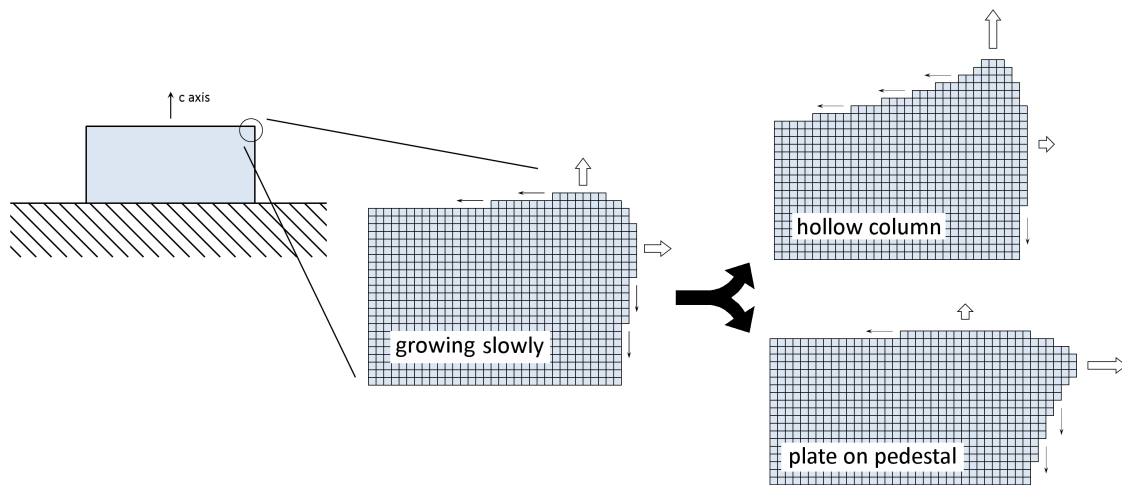


Figure 2: A schematic depiction of the SDAK instability described in the text. The growth of the corner of a faceted ice crystal prism (left) is dominated by the nucleation of terraces on the basal and prism facets (center). If the nucleation rate increases as the width of the top basal terrace decreases (top right), in keeping with the SDAK model, then the accelerated growth narrows the basal surface, accelerating the growth still more. The resulting positive feedback generates the growth of a hollow columnar crystal. If the same SDAK effect is more prevalent on the prism facet (lower right), then the instability leads to the growth of a thin plate from the top edge of the prism.

increasing surface curvature, following from simple surface energy considerations [16]. How the step energy, and thus  $\sigma_0$ , becomes altered on a thin molecular terrace is a more complex and somewhat orthogonal question. At the molecular level, these phenomena may all be interconnected, but these connections are not yet known from our present understanding of the ice surface structure and dynamics.

For the present discussion we treat the SDAK model as a hypothesis to be tested by observations. Our goal is then to examine whether this hypothesis fits experimental data, and to use additional measurements and modeling to better understand how structure-dependent attachment kinetics affects ice crystal growth dynamics.

## 2.4 An Edge-Enhancing SDAK Instability

An important feature of the SDAK hypothesis is that it leads to an edge-enhancing growth instability. The essential mechanism is that as a thin edge begins to form,  $\sigma_0$  decreases and thus further increases the edge growth rate. The enhanced growth causes the edge to sharpen, which again increases the growth rate. This positive feedback yields a growth instability that enhances the formation of sharp edges.

To examine the instability in more detail, consider the growth of an initially isometric prism on a substrate, depicted in Figure 2. We assume the presence of an inert background gas surrounding the crystal, so the growth is partially diffusion limited. If the crystal is growing slowly (center

diagram in the figure), then molecular terraces nucleate slowly near the corner of the crystal, where the supersaturation is highest, and steps propagate away from the corner. The corner itself is rounded from the Gibbs-Thomson effect. For slow growth, this is essentially the standard model of diffusion-limited faceted crystal growth, resulting in slightly concave faceted surfaces.

Consider now the top terrace on either side of the growing corner. As the supersaturation is increased, terraces nucleate more frequently, so the average width of the top terrace decreases. As the SDAK effect reduces  $\sigma_0$  on the narrower terraces, the nucleation rate increases and in turn the more rapid growth further decreases the width of the top terrace.

At this point a competition occurs between growth on the basal and prism facets, as shown in the pair of diagrams on the right side of Figure 2. If the SDAK effect preferentially reduces  $\sigma_0$  on the basal facet (top right diagram), then the basal growth is especially enhanced. Because the growth is also diffusion-limited, the fast growth on the basal facet depletes the water vapor supply from the nearby prism facet. This decreases the nucleation rate on the prism facet, which causes the average width of the last terrace to increase, which in turn increases  $\sigma_{0,prism}$ . The combined effect is that  $\sigma_{0,prism}$  increases to its intrinsic value while  $\sigma_{0,basal}$  grows ever smaller as the basal edge grows sharper. The final result is a hollow column morphology with thin basal edges. Alternatively, the same instability could favor the prism facets, as seen in the lower right diagram in Figure 2. In this case a thin plate-like crystal would form on the isometric prism, producing a “plate-on-pedestal” (POP) morphology, described in more detail below.

Note that the SDAK instability nicely explains the abrupt transitions between plate-like and columnar growth seen in the morphology diagram. Relatively small changes in the surface attachment kinetics with temperature can be amplified via the SDAK instability to yield very substantial changes in the final crystal morphologies.

Note also that the SDAK instability is essentially an extension of the well-known Mullins-Sekerka instability in diffusion-limited growth [17]. The latter is well known for producing dendritic branching during solidification, but alone it does not automatically explain the formation of thin plate-like or hollow columnar crystals. From our diffusion modeling of crystal growth, we have found that these thin-edge morphologies require strong anisotropies in the attachment kinetics – namely  $\alpha_{prism} \gg \alpha_{basal}$  for thin plates or  $\alpha_{prism} \ll \alpha_{basal}$  for hollow columns. The SDAK instability provides a natural mechanism to generate these strong anisotropies.

### 3 Experimental Evidence for the SDAK Model

The first piece of evidence supporting the SDAK hypothesis is simply the disagreement between measurements of the intrinsic  $\alpha(\sigma_{surf}, T)$  and the morphology diagram, as described above. The SDAK mechanism nicely explains the formation of thin plates at -15 C, for example, which is otherwise difficult to reconcile with the measured  $\alpha_{basal}(\sigma_{surf})$  and  $\alpha_{prism}(\sigma_{surf})$  at that temperature. Another piece of supporting evidence is the observation of abrupt morphological transitions between plate-like and columnar forms in the morphology diagram, which again is naturally explained by the SDAK model.

These pieces of evidence provide only indirect support for the SDAK model, however, based mainly on morphological observations. Quantitative modeling of growth data provides a much stronger confirmation, as we demonstrate below. Detailed measurements and diffusion modeling of growth behaviors at -15 C fit the SDAK model well, while we see no easy way to explain the data without invoking the SDAK effect.

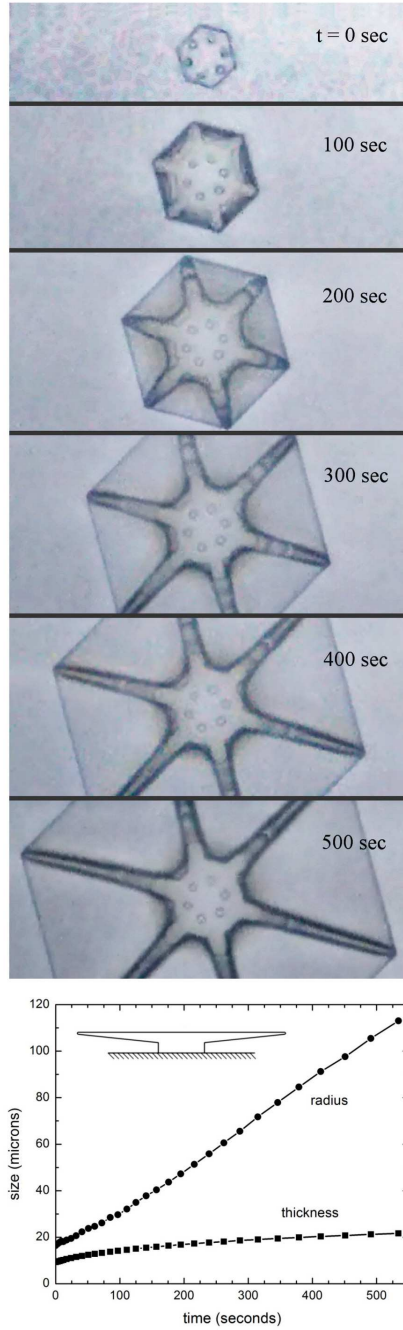


Figure 3: An example of “Plate-on-Pedestal” (POP) crystal growth at -15 C. The top series of images shows the development of a thin sectored plate on top of an initial hexagonal prism. The graph shows measurements of the plate radius and central thickness as a function of time. The inset diagram in the graph shows the inferred cross section of the crystal at  $t = 500$  seconds.

### 3.1 Plate-on-Pedestal Growth

The clearest experimental evidence we have found to date supporting the SDAK hypothesis comes from observations of what we call “plate-on-pedestal” (POP) crystal growth, and an example is shown in Figure 3. The top image at  $t = 0$  in this figure shows a small ice crystal with one basal facet resting on a sapphire substrate. The initial morphology was essentially that of a simple hexagonal prism, but with six small pits on one basal facet. These surface features were trapped against the substrate, as evidenced by the fact that they remained essentially unchanged during the subsequent growth of the crystal.

The substrate and test crystal in Figure 3 lie at the bottom of a small growth chamber. The top of the chamber is an ice reservoir (IR) consisting of another sapphire surface covered with small ice crystals. The IR provides a source of water vapor for the test crystal, and the temperature difference  $T_{IR} - T_{subst}$  determines the supersaturation far from the test crystal, which we denote as  $\sigma_\infty$ . Additional experimental details can be found in [15]. In these experiments the test crystal is small enough, and the ice thermal conductivity is high enough, that the temperature of the test crystal is essentially equal to  $T_{subst}$ .

At  $t = 0$  in Figure 3, the supersaturation was increased from  $\sigma_\infty = 0$  to  $\sigma_\infty = 8$  percent, in an atmosphere of air at a pressure of one bar. By  $t = 100$  seconds, a thin plate had begun growing from the top edge of the prism, and this plate grew larger with time. The ridges dividing the plate into six sectors formed on the underside of the plate (i.e., the side of the plate nearest the substrate). Ridging of this kind is commonly seen in the growth of plate-like ice crystals from water vapor [7]. The graph in Figure 3 shows the radius (here defined as half the distance between opposite prism facets) and thickness (equal to the distance from the substrate to the center of the upper basal facet) of the crystal as a function of time. The thickness was measured using optical interferometry as described in [15], while the radius was determined from the optical images. The inset in the graph shows the approximate cross section of the crystal at  $t = 500$  seconds. The detailed morphology of the ridging was not measured, and the top surface of the plate may be slightly conical in shape, and thus not precisely flat as indicated in the inset cross-section diagram.

The POP morphology shown in Figure 3 was observed at  $-15^\circ\text{C}$  as long as  $\sigma_\infty$  was above about 4-5 percent (depending on the initial crystal radius and thickness). For lower  $\sigma_\infty$ , simple prisms grew and the POP morphology did not develop. For these low- $\sigma_\infty$  crystals, the prism growth was additionally influenced by substrate interactions. The presence of chemical residue on the substrate (even after thorough cleaning) often lowered the nucleation barrier on facets intersecting the substrate, resulting in growth rates that were somewhat higher than one would expect from the intrinsic  $\alpha$  measurements in Figure 1. This effect is discussed further in [15], but it played only a minor role in the current measurements.

Note that the POP morphology also does not appear when the background pressure is low. The measurements yielding the results in Figure 1 were taken at pressures below 30 mbar, where diffusion is rapid and the growth is mainly kinetics limited. In general the crystal morphology is more complex at higher pressures and for larger crystals [18], a fact that follows from scaling relationships in solutions to the diffusion equation [19].

Before considering a quantitative analysis of the growth of POP crystals, we first examine the growth of simple prism crystals, and an example is shown in Figure 4. In this figure, the data points show measurements of the radius and thickness of the crystal as a function of time, similar to the data shown in Figure 3, also taken in air at a pressure of one bar. For this crystal, however, the supersaturation was only  $\sigma_\infty = 3$  percent, so the growth was slower and the POP morphology



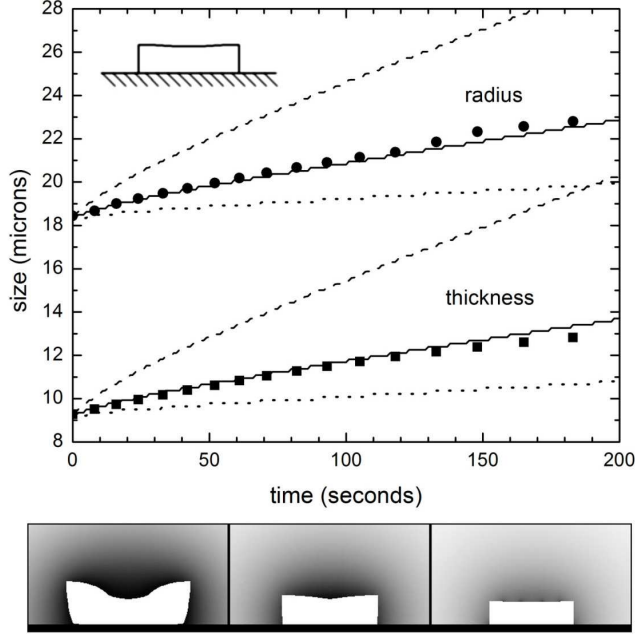


Figure 4: Modeling the growth of a relatively simple prism crystal. Data points show measurements of the radius and central thickness of the crystal as a function of time, and the applied supersaturation was  $\sigma_\infty = 3$  percent. Lines show numerical models of the growth using  $\alpha = \exp(-\sigma_0/\sigma_{surf})$  with  $\sigma_{0,basal} = \sigma_{0,prism} = 2$  percent. The dashed lines, solid lines, and dotted lines indicate models with  $\sigma_\infty = 3, 1.5$ , and  $0.75$  percent, respectively. The inset in the graph shows the inferred cross section of the crystal at 200 seconds. The images below the graph show cross sections calculated in the three models at 200 seconds, with  $\sigma_\infty$  decreasing from left to right. In these images the crystal is shown in white, and the brightness of the surrounding area is proportional to the supersaturation field.

did not develop. The crystal showed a slight basal hollowing at  $t = 200$  seconds, as shown in the cross-section diagram inset in the graph.

Diffusion modeling was performed using the cylindrically symmetrical cellular automaton model described in [19]. The outer radial surface in this model corresponds to a single prism “facet,” which we found to be an adequate geometrical approximation to the six prism facets of a simple hexagonal prism. In addition to simple prisms, hollow columns and POP morphologies can also be effectively modeled with this cylindrically symmetrical method.

For the models shown in Figure 4 and in subsequent figures below, the outer boundary with  $\sigma = \sigma_\infty$  was set at  $r_{outer} = 105 \mu m$  and  $z_{outer} = 75 \mu m$ . The diffusion equation was solved in the space surrounding the crystal to determine the supersaturation field  $\sigma(r, z)$ , with input  $\alpha_{basal}(\sigma_{surf})$  and  $\alpha_{prism}(\sigma_{surf})$  for the facet surfaces, assuming  $\alpha = 1$  at kink sites on the surface [19]. The quantitative accuracy of the modeling software was thoroughly tested using analytic solutions for the growth of spherical and infinite cylindrical crystals.

We believe we have a reasonable understanding of the factor-of-two discrepancy between the data taken at  $\sigma_\infty = 3$  percent and the best-fit model with  $\sigma_\infty = 1.5$  percent (see Figure 4). About half of the discrepancy arises from the model itself. Part comes from the fact that the outer boundaries in the model are fairly close to the crystal, which causes the model to grow more rapidly than it would if the boundaries were as far away as in the experiment. Another part comes from our choice for the adaptive time steps in the model [19]. With longer time steps, the supersaturation field does not have time to relax fully as the crystal grows, again causing the model crystal to grow too fast. Both these effects were investigated using analytic solutions, and a compromise between modeling accuracy and speed was made.

Even using shorter time steps and more distant outer boundaries, however, we could not obtain a good fit to the data using a model input of  $\sigma_\infty = 3$  percent. We believe the remainder of the discrepancy was caused by distant neighboring crystals in the experiment. These additional crystals act as water vapor sinks, reducing the supersaturation around the crystal by a small amount, and this effect apparently caused an effective  $\sigma_\infty$  that was roughly 30 percent lower than that calculated from  $T_{IR} - T_{subst}$ . We believe that the combined effects of these modeling and experimental systematics reasonably explain the factor of two discrepancy between the applied  $\sigma_\infty$  in the experiment and the best fit model.

With the crystal in Figure 4 and others, we found that a good modeling strategy was to adjust the assumed  $\sigma_\infty$  values in the model to match the overall growth rates observed. This seemed to adequately fit for both the modeling and experimental systematics in  $\sigma_\infty$  without adverse effects. Typically the best fit  $\sigma_\infty$  value was about a factor of two below the experimental value determined from  $T_{IR} - T_{subst}$ , with some crystal-to-crystal variation reflecting differences in experimental conditions.

Figure 5 shows additional modeling of the same low- $\sigma_\infty$  crystal shown in Figure 4. Here we see that a model with  $\sigma_{0,prism} = 3$  percent – the preferred value from the intrinsic data in Figure 1 – yields prism growth that is too slow and basal growth that is too fast, along with too much hollowing in the basal facet. In contrast, the model with  $\sigma_{0,prism} = 1$  percent yields prism growth that is too fast and basal growth that is too slow, along with the beginnings of a POP-like morphology. The model with  $\sigma_{0,prism} = 2$  percent matches the data reasonably well. The fact that the best fit value of  $\sigma_{0,prism} = 2$  percent does not agree with intrinsic growth measurements was not unexpected, given the known influence of substrate interactions mentioned above.

Our conclusions from this modeling exercise include: 1) our numerical methods produce adequate quantitative models of the growth of simple prism crystals, 2) adjusting  $\sigma_\infty$  is a reasonable strategy to fit the overall growth rates, 3) a value of  $\sigma_{0,basal} \approx 2$  percent, consistent with the intrinsic growth rate shown in Figure 1, gives a reasonable fit to the data, and 4) a value of  $\sigma_{0,prism} \approx 2$  percent, likely decreased from its intrinsic value by substrate interactions, is needed to reproduce the growth of this low- $\sigma_\infty$  crystal. The significance of this latter result becomes apparent when we compare it with models of the growth of a POP crystal.

Figure 6 shows the growth of a second example crystal, similar to the results in Figure 4 but with a higher applied supersaturation of  $\sigma_\infty = 10$  percent. Modeling proceeded as before, and we see that again the overall growth scales with  $\sigma_\infty$ , giving a best fit  $\sigma_\infty$  that is once more about a factor of two smaller than the experimentally calculated supersaturation. And again we see that adjusting  $\sigma_\infty$  in the models allows us to reasonably fit the overall morphology as well as the quantitative growth measurements.

Figure 7 shows another comparison of three models, this time keeping  $\sigma_\infty = 5$  percent and  $\sigma_{0,basal} = 2$  percent, while varying  $\sigma_{0,prism}$ . Here we see that the basal growth depends only weakly

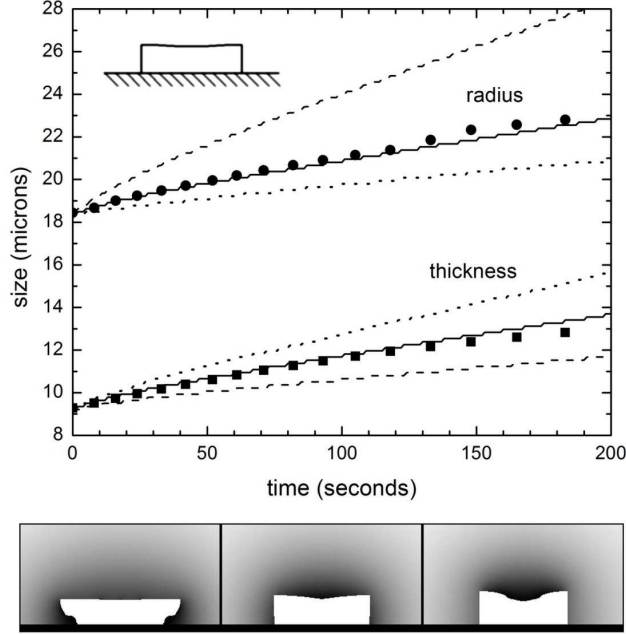


Figure 5: Additional modeling of the same low- $\sigma_\infty$  crystal shown in Figure 4. In these models we fixed  $\sigma_\infty = 1.5$  percent while keeping  $\sigma_{0,basal} = 2$  percent. The dashed, solid, and dotted lines show models with  $\sigma_{0,prism} = 1, 2$ , and  $3$  percent, respectively. Images below the graph again show model cross sections, with  $\sigma_{0,prism}$  increasing from left to right.

on our choice for  $\sigma_{0,prism}$  (over this range), while changing  $\sigma_{0,prism}$  affects the radial growth rate and the overall POP morphology.

Note that we did not attempt to construct a numerical model that included the full SDAK effect. Our models were more basic in that they assumed attachment coefficient functions  $\alpha_{basal}(\sigma_{surf})$  and  $\alpha_{prism}(\sigma_{surf})$  that did not depend on the structure of the crystal. This was appropriate for low- $\sigma_\infty$  crystals, where the SDAK effect was absent, but the models also worked quite well for describing POP crystals. The thin edge developed very quickly on the high- $\sigma_\infty$  crystal in Figures 6 and 7, and the subsequent plate growth was determined mainly by  $\alpha_{prism}$  on the edge. The only other prism facets present were on the pedestal, and these surfaces were so heavily shielded that their growth was slow regardless of  $\alpha_{prism}$ . For the specific POP geometries we observed, therefore, our basic models yielded essentially the same quantitative growth behavior as we would have obtained with a full SDAK model.

### 3.2 Conclusions

We draw several conclusions from a comparison of the growth of these two crystals: 1) changing  $\sigma_\infty$  in the models changes the overall growth rates of the crystals, as one would expect. Adjusting the model  $\sigma_\infty$  to be about half the experimental  $\sigma_\infty$  gives a good fit to the data, and the need for this

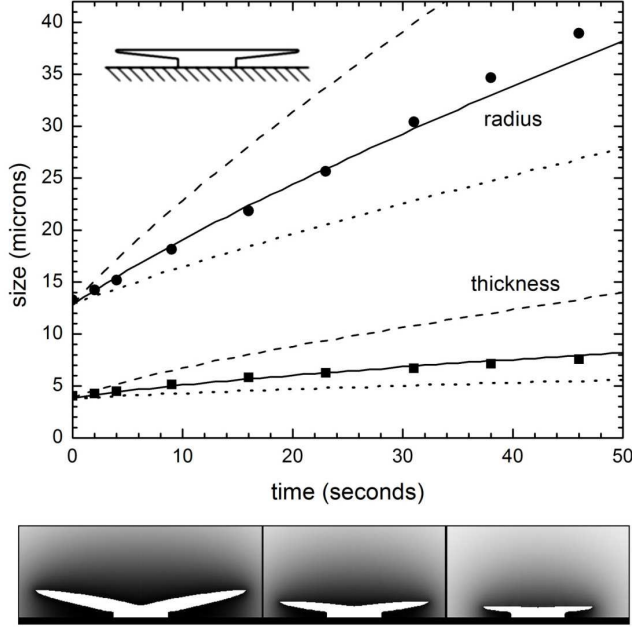


Figure 6: An example of the growth of a POP crystal with an applied supersaturation of  $\sigma_\infty = 10$  percent. This crystal began at  $t = 0$  with a simple prism morphology, then quickly developed a POP morphology. The points in the graph show the measured plate radius and central crystal thickness as a function of time. The inset diagram shows the inferred crystal cross section at 50 seconds. The dashed, solid, and dotted lines show models with  $\sigma_\infty = 10$ , 5, and 2.5 percent, respectively, using  $\sigma_{0,basal} = 2$  percent and  $\sigma_{0,prism} = 0.3$  percent. The images below the graph show the corresponding model cross sections at 50 seconds.

factor of two is reasonably well understood; 2) a value of  $\sigma_{0,basal} = 2$  percent gives a reasonable fit to all the data, and this value is consistent with the intrinsic growth measurements in Figure 1; and 3) the low- $\sigma_\infty$  prism crystal requires  $\sigma_{0,prism} \approx 2$  percent to fit the data, while the high- $\sigma_\infty$  POP crystal requires  $\sigma_{0,prism} \approx 0.3$  percent.

We observed numerous other crystals in addition to these two examples, and the overall growth behaviors are consistent, leading to essentially the same conclusions. Each observed crystal had a different initial radius and thickness, plus the supersaturation and substrate interactions differed slightly from run to run. For this reason we found it advantageous to present case studies of these two example crystals.

The most significant conclusion from these data is that it was clearly not possible to model both crystals adequately using a single-valued function  $\alpha_{prism}(\sigma_{surf})$  for the prism attachment coefficient. This is perhaps most clearly seen by examining the prism growth velocities as a function of  $\sigma_{surf}$ , as the latter can be obtained from the best-fit models. For the low- $\sigma_\infty$  crystal at  $t = 200$  seconds, we found a maximum value of  $\sigma_{surf} \approx 0.51$  percent on the prism facet, yielding a growth rate of  $v_{prism} \approx 20$  nm/sec. For the high- $\sigma_\infty$  crystal at  $t = 50$  seconds, we found a maximum  $\sigma_{surf} \approx 0.67$

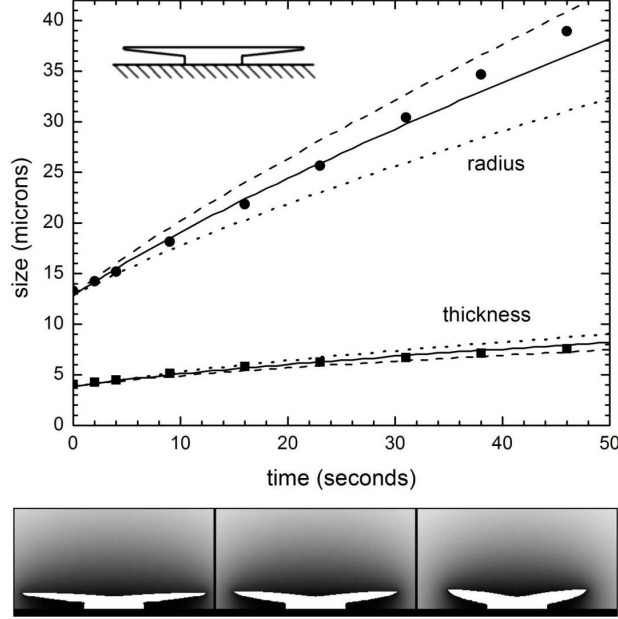


Figure 7: Additional models of the same high- $\sigma_\infty$  shown in Figure 7. For these models we fixed  $\sigma_\infty = 5$  percent and  $\sigma_{0,basal} = 2$  percent. The dashed, solid, and dotted lines show models with  $\sigma_{0,prism} = 0.15, 0.3$ , and  $0.6$  percent, respectively.

percent on the edge of the plate, yielding a growth rate of  $v_{prism} \approx 560$  nm/sec. Although the supersaturations at the prism surfaces in these crystals differed only slightly, the thin edge of the POP crystal grew nearly 30 times faster.

The impact of this result becomes apparent when one tries to produce quantitative models of the growth behavior without invoking the SDAK hypothesis. We examined a number of different crystals and explored different modeling strategies, but in the end the conclusion was robust and clear – the attachment kinetics on the edge of the thin plate was much faster than on the edge of a thick plate. These measurements strongly supports the SDAK hypothesis, and we could not find another reasonable hypothesis that would quantitatively explain the data.

### 3.3 SDAK or VDAK?

One alternative hypothesis we explored in some detail was *velocity-dependent attachment kinetics* (VDAK), which in this case assumes  $\alpha_{prism}$  can depend on the surface growth velocity. The VDAK hypothesis is motivated by kinetic roughening [16], and we consider VDAK as a generalization of this phenomenon. In a nutshell, kinetic roughening describes a process where sufficiently fast crystal growth causes the growing surface (normally faceted) to become disordered at the molecular scale, with a resulting jump in the attachment kinetics. For the case of POP crystal growth, assuming a VDAK hypothesis implies that the edge of the thin plate is growing sufficiently fast to produce a

partial roughening, and thus an increase in  $\alpha_{prism}$  on the edge.

The VDAK hypothesis could perhaps explain the POP data above, but it also leads to other testable predictions that we found were not verified by experiment. The first prediction would be a jump in the growth rate once a critical growth velocity is exceeded. This jump would indicate a VDAK transition, and the jump should occur on large faceted surfaces as well as on thin edges. And, importantly, the jump should occur both with or without a background gas.

A second prediction is that the VDAK hypothesis should lead to a different kind of growth instability. When  $\sigma_{surf}$  is increased and the attachment kinetics starts to increase from the VDAK effect, this should in turn increase the growth velocity for the same  $\sigma_{surf}$ , thus further increasing the attachment kinetics. This positive feedback would likely result in a rapid jump to fully roughened growth with  $\alpha \approx 1$ . Again we would expect this instability to occur on large facets or thin edges, with or without a background gas.

Thus the VDAK instability should result in a hysteresis behavior in growth measurements. Increasing and then decreasing  $\sigma_{surf}$  should lead to a growth velocity  $v(\sigma_{surf})$  that is a double-valued function of  $\sigma_{surf}$  – low for increasing  $\sigma_{surf}$  and higher for decreasing  $\sigma_{surf}$ , as long as the critical velocity is exceeded at some point.

We tested these predictions by measuring prism facet growth as a function of  $\sigma_{surf}$  at  $T = -15$  C with a background pressure of air at 20 mbar, in a fashion similar to the experiments described in [15]. The main changes were that we pushed the growth to much higher peak velocities, and we quickly ramped  $\sigma_{surf}$  up and then down, measuring the prism growth rate in the process. An example crystal from this set of measurements is shown in Figure 8.

Graph (b) in Figure 8 shows several significant things: 1) we observed no jump in growth as a function of  $\sigma_{surf}$ , even though the peak velocity was over 800 nm/sec, faster than the growth velocities observed in the POP crystals above; 2) the observed  $v(\sigma_{surf})$  was consistent with the intrinsic growth measurements shown in Figure 1; and 3) we observed no hysteresis in  $v(\sigma_{surf})$  – the measured velocities with  $\sigma_{surf}$  increasing were not significantly different from the velocities with  $\sigma_{surf}$  decreasing.

The data shown in Figure 8 show no evidence of any of the expected VDAK effects, so we conclude that the VDAK hypothesis is refuted by these data. If a VDAK effect does exist, it seems to play no significant role in the prism facet growth at -15 C. Note that again we observed more than the single crystal shown in Figure 8, and the overall conclusions were quite robust.

### 3.4 Hysteresis in Plate-on-Pedestal Growth

Although we did not observe any hysteresis behavior that could be ascribed to VDAK effects, we did observe a clear hysteresis behavior in the growth of POP crystals, and an example from this set of measurements is shown in Figure 9. These data were acquired by slowly increasing  $\sigma_{\infty}$  while observing the development of a POP crystal at -15 C in a background of air at a pressure of one bar. Additional experimental details, and additional observations, can be found in [20].

In Figure 9 we see that the initial growth of this crystal, while  $\sigma_{\infty}$  was small and slowly increasing, produced a nearly isometric simple prism. In this case the prism growth velocity,  $v_{prism}$ , was roughly 1.5 times the basal growth velocity,  $v_{basal}$ . This factor was likely affected by substrate interactions that influenced the prism growth. As  $v_{prism}$  approached 200 nm/sec, the POP morphology began to form. This event in turn caused  $v_{prism}$  to jump to about 700 nm/sec while  $v_{basal}$  remained essentially constant.

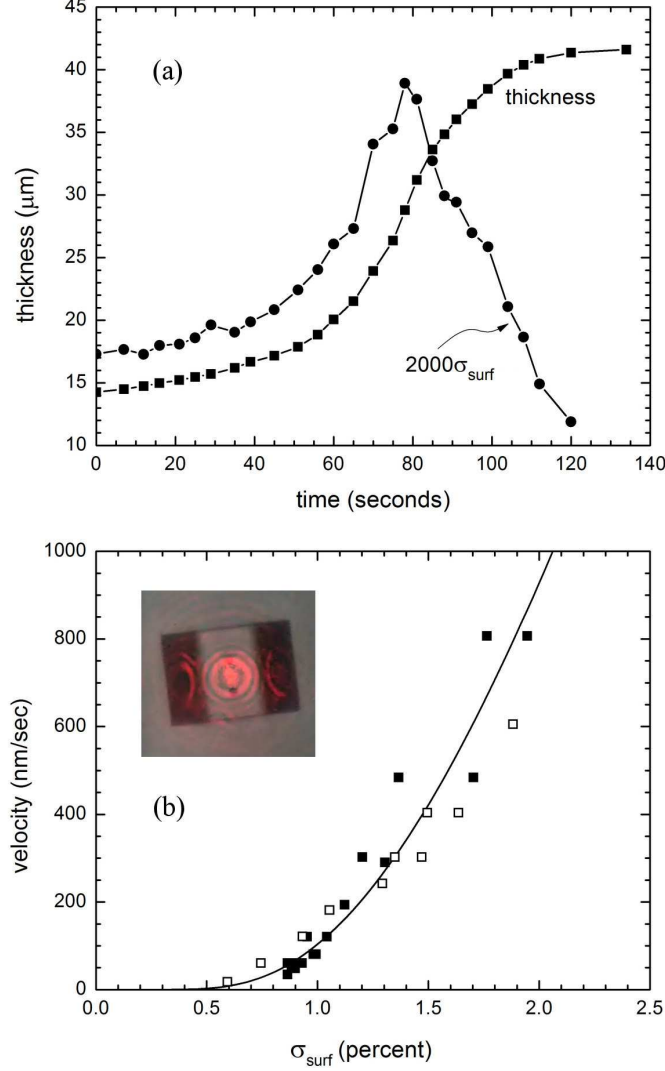


Figure 8: A measurement of prism facet growth at -15 C in a background of air at a pressure of 20 mbar. In (a) we present measurements of the crystal thickness (defined here as the distance from the substrate to the top prism facet) as a function of time. The supersaturation at the surface is also plotted, scaled to  $2000\sigma_{\text{surf}}$  to fit on the graph. In (b) the measured prism growth velocity is plotted as a function of  $\sigma_{\text{surf}}$ . Solid points give  $v(\sigma_{\text{surf}})$  as  $\sigma_{\text{surf}}$  was being increased; open points show  $v(\sigma_{\text{surf}})$  as  $\sigma_{\text{surf}}$  was being decreased. The line shows  $v = \alpha v_{\text{kin}} \sigma_{\text{surf}}$  with  $\alpha = \exp(-\sigma_0/\sigma_{\text{surf}})$  and  $\sigma_0 = 3$  percent. The inset image in (b) shows the test crystal at the end of the run. Oscillations in the brightness of the laser spot were used to interferometrically measure the crystal thickness. In both these plots,  $\sigma_{\text{surf}}$  includes a correction to remove residual diffusion effects. A description of this correction, along with additional experimental details, can be found in [15].

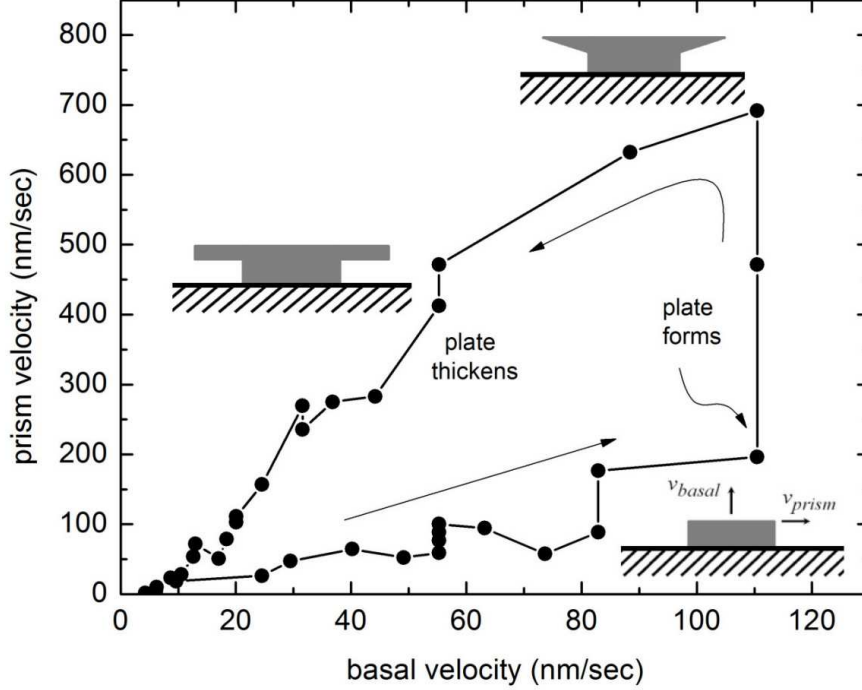


Figure 9: An example showing hysteresis in POP crystal growth, here plotting  $v_{prism}$  versus  $v_{basal}$  as the crystal grew. The initial growth (lower track in the measured points) exhibited a simple prism morphology (lower right inset diagram) as  $\sigma_\infty$  was slowly increased, with  $v_{prism} \approx 1.5v_{basal}$ . When the plate formed,  $v_{prism}$  abruptly increased while  $v_{basal}$  remained constant (top inset diagram). Beginning at the  $v_{prism}$  peak,  $\sigma_\infty$  was slowly decreased, causing both  $v_{prism}$  and  $v_{basal}$  to decrease as the plate edge thickened (left inset diagram).

Once the plate had fully formed,  $\sigma_\infty$  was then slowly decreased with time. This caused both  $v_{basal}$  and  $v_{prism}$  to decrease, and it caused the edge of the plate to slowly thicken. However, the growth in the  $v_{basal}$ - $v_{prism}$  plane did not track back down its original path. Instead the prism growth remained high, with  $v_{prism} \approx 8v_{basal}$ .

Simple diffusion modeling with fixed  $\alpha_{basal}(\sigma_{surf})$  and  $\alpha_{prism}(\sigma_{surf})$  cannot reproduce this hysteresis behavior, but it is easily explained with the SDAK model. During the initial stages of growth, when  $\sigma_\infty$  was fairly low, the crystal morphology was that of a simple prism, so there was no SDAK effect. When the growth passed a threshold, the SDAK instability caused a thin plate to form on the prism, and the accompanying decrease in  $\sigma_{0,prism}$  resulted in a jump in  $v_{prism}$ . The supersaturation near the crystal surface remained approximately constant during this process, as evidenced by the fact that  $v_{basal}$  did not change appreciably during the jump in  $v_{prism}$ .

As  $\sigma_\infty$  was subsequently reduced, the SDAK instability began to lose its strength, causing the plate to thicken. As the plate slowly thickened,  $\sigma_{0,prism}$  slowly increased back to its intrinsic value. The initial jump in  $v_{prism}$  was rapid because it took little time for the SDAK instability to sharpen



the edge of the plate. The subsequent decrease in  $v_{prism}$  took longer because it took more time for the plate to thicken substantially.

The hysteresis behavior shown in Figure 9 is nicely explained by the SDAK instability, so it provides additional supporting evidence for the SDAK hypothesis. However the experiment was somewhat complex and difficult to model accurately, while the underlying growth behavior is essentially the same as with other POP crystals. Therefore we found that the constant- $\sigma_\infty$  measurements described above provided better quantitative support for the SDAK hypothesis.

### 3.5 Additional SDAK Support

The SDAK instability is most clearly seen in ice plate growth at -15 C, and to date we have not mapped out the growth dynamics at other temperatures. Nevertheless, quantitative modeling of the growth of ice crystals in free fall [21, 22] does suggest that SDAK effects are also present in the growth of columnar crystals near -5 C and in plate growth at -2 C. Thus our preliminary investigations suggest that SDAK effects in ice growth are substantial over a broad temperature range.

The SDAK instability may also explain the recent observations of fast-growing needle-like structures alongside faceted crystals at -5 C reported by Knight [23]. Here again, the simultaneous occurrence of these quite different morphologies is a natural result of the SDAK instability, but is otherwise difficult to explain.

## 4 Discussion

Progress toward understanding the formation of complex structures during solidification has generally been hard won, as numerous physical processes are involved over many length scales. Creating even qualitative models of the subtle many-body dynamics governing crystal growth is difficult, and realizing accurate numerical models that allow quantitative comparison with experimental data remains a significant challenge.

It has been known since the mid-1960s, for example, that branched structures arise from the Mullins-Sekerka instability during diffusion-limited growth. Producing a quantitative model of this process required substantial theoretical effort, however, culminating in the development of solvability theory during the 1980s [1, 2]. With this we learned that the overall branching scale is set by seemingly minor anisotropies in the surface dynamics. The surface energy anisotropy plays the key role in the case of solidification from the liquid phase, while for solidification from gaseous precursors the anisotropy in the surface attachment kinetics is generally the more dominant factor [7].

Numerical models of diffusion-limited growth were developed in conjunction with solvability theory, including front-tracking and phase-field techniques. These have enjoyed reasonable success in reproducing the salient features observed in many liquid systems aimed at understanding metallurgical solidification processes. These same numerical techniques have been generally less successful modeling growth from the vapor phase, however, including ice crystal growth, when the resulting structures are both faceted and branched. For these systems, diffusion models derived from cellular automata have proven more successful in reproducing observed structures [24]. Understanding the differences in these numerical modeling techniques, and producing quantitative models with more accurate surface physics, remains an area of current research.

Analysis of diffusion-limited growth using these theoretical tools has yielded numerous insights into the dynamics of structure formation. For the case of ice, the increase in morphological complexity with increasing supersaturation is reasonably well understood at a qualitative level, although quantitative details are still lacking. Solvability theory nicely explains how the tip velocity of a growing dendritic structure depends linearly on supersaturation for solidification from vapor, while a quadratic dependence on undercooling is typical for growth from the liquid phase [7]. Furthermore, scaling relationships in diffusion growth models provide an explanation for the increase in structural complexity that accompanies decreasing diffusion rates [19].

In spite of these numerous successes in growth modeling, many puzzles still remain in understanding the detailed physics underlying the surface attachment kinetics, especially in growth from the vapor phase when attachment kinetics plays a substantial role. In the case of ice growth, the problem is made considerably more difficult by the presence of surface melting, since it is still largely unknown how this phenomenon influences crystal growth dynamics.

Several experiments from recent years have indicated that faceted ice growth is well described by a dislocation-free layer-nucleation model ([12], and references therein). Quantitative measurements have further shown that the attachment coefficients on the principal facets can be parameterized using  $\alpha(\sigma) = A \exp(-\sigma_0/\sigma)$ , with the measured  $A(T)$  and  $\sigma_0(T)$  shown in Figure 1. Classical nucleation theory then allows one to convert  $\sigma_0(T)$ , a complex dynamical quantity, into the step energy  $\beta(T)$ , a more basic equilibrium property of the ice surface.

With the experimental and modeling results presented above, we have added a new twist to our understanding of crystal growth dynamics, namely structure-dependent attachment kinetics and the SDAK instability. Our data and modeling indicate that the SDAK effect is a necessary ingredient for reproducing the observed growth behavior of ice from water vapor at -15 C, and it appears likely that the formation of columnar structures near -5 C and plate-like forms near -2 C are also influenced by this phenomenon. We believe, therefore, that the SDAK model described above represents a substantial step forward in explaining the overall organization in the Nakaya morphology diagram. It appears promising that additional features in the model will emerge from future targeted experimental studies.

Ongoing studies of ice growth from water vapor are revealing ever more features in an already rich phenomenology, and our list of observed growth instabilities now includes the Mullins-Sekera instability, the SDAK instability, and the electric growth instability [25]. To these we add the rather complex behavior seen in the attachment kinetics, notably different on the two principal facets, and it becomes clear that this particular system still has much to teach us about the subtle interplay of different physical processes governing crystal growth dynamics.

Experimental and theoretical efforts focusing on structure formation in ice over the past several decades have continually pushed the remaining frontiers ever closer to the molecular scale. The SDAK instability, the parameterization of the attachment coefficients for the principal facets, as well as the properties of surface melting, all arise from the detailed molecular dynamics at the crystal surface. Since much progress has been made recently in molecular dynamics simulations of the ice surface [26, 27], it appears promising that additional investigations along these lines may reveal new insights into ice growth behavior, and especially why the ice surface properties vary with temperature as they do. How these advances apply to other crystal systems, and to our understanding of surface molecular dynamics in general, remains to be seen.

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